

# PATENT SPECIFICATION

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## (54) PRODUCTION OF AN IMPROVED FINISH IN TEXTILE PRODUCTS

- (71) We, INTERCOOPERATION KERESKEDELEMFEJLESZTÉSI RT., of 14, Attila ut, Budapest I, Hungary, a body corporate organized under the laws of Hungary, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The invention concerns a process for the production of a finish of layered structure and heterogeneous distribution developed on filaments of cellulosic fibrous materials, yarns or woven or knitted fabrics, or for example
- 15 cellulosic textile products mixed with synthetic filament materials, with the aid of which the dry and wet crease recovery and the dimensional stability of the listed products may be significantly increased, and their abrasion
- 20 resistance or tearing strength may be considerably improved, relative to known finishes of similar intended use.
- It is known that the dry and wet recovery of textile products of cellulose based single-
- 25 component filamentary materials, or of such materials mixed with synthetic filamentary materials, is limited. In order to improve the crease recovery, one proceeds by cross-linking the cellulose itself or by applying a cross-
- 30 linkable material to the cellulose. It is characteristic of such finishing treatments that the tendency for resilient shape recovery of cellulose-based products is improved, but the tearing strength and abrasion resistance considerably deteriorate.
- 35 The technical aim sought to be attained, i.e. the improvement of crease recovery and dimensional stability without appreciable deterioration of abrasion resistance and tearing strength could in principle be achieved with a heterogeneous finish which is capable of simultaneously satisfying these partially
- 40 mutually contradictory requirements. As witnessed by the technical literature, recently numerous proposals have been made with which the desired aims may be achieved only partially but not to a sufficient extent or only by employing very expensive means; in other words experiments performed to develop
- 45 layers of heterogeneous structure have not so far assured the desired result.
- In effect, the reduction of abrasion resistance may be attributed to the condensed or cross-linked synthetic resin layer applied to the outer surface of the filament,
- 50 the formation of which layer is required from the point of view of dimensional stability and crease recovery in the textile material. However, no known proposal has been successful in obviating the attendant deterioration in abrasion resistance and tearing strength, and consequently requirements regarding crease recovery, resilience and dimensional stability
- 55 have been met only at the expense of wear resistance and tearing strength of textile products.
- Several research workers have been engaged in transforming the surface layer of textile products to be treated. A. W. Reeves (Amer. Dyestuff Rep. 57, 37—41 /1968/)
- 60 sought to solve the transformation of surface layer by applying polymers to the surface of the fabric.
- Authors Gogek and Valkó (Textilveredlung 2, 423—428 /1967/) performed
- 65 numerous experiments to produce a cross-linking agent of heterogeneous distribution to be formed in the textile product and unambiguously ascertained that this could not be achieved in an aqueous medium. For removing the water-soluble, cross-linkable monomer applied to the filament surface they employed a mixture of water and ethyl alcohol or water and acetone. Another of
- 70 their proposed solutions is that they wished to prevent cross-linking by an anti-catalyst slowly diffusing into the filament, or by de-
- 75
- 80
- 85

activating the acidic catalysts by an alkaline solution in aqueous alcohol.

- 5 A. E. Lauchenauer and his collaborators (Text. Res. J. 39, 585—603 /1969/) de-  
activated the catalyst on the filament surface  
with ammonia. According to the experiments  
of authors Meier and Zollinger (Textilvered-  
lung 5, 709—720 /1970/) the catalyst in the  
10 outer layer of the filament may be disabled  
by triethylene tetramine in a polar solvent.  
Author J. Willard and his collaborators  
(Text. Res. J. 39, 413—421 /1969/) de-  
veloped a process for directional cross-link-  
ing achievable in the core of the cotton fila-  
15 ment by solubilizing the cross-linking mono-  
mer before condensation from the outer layer  
of the filament by means of an organic  
solvent.

- 20 None of the listed methods has found  
significant or widespread use in industry.

- The aim of the present invention is the  
production, by relatively simple technological  
means, of a synthetic resin finish on cellulosic  
25 filament textile products which is of hetero-  
geneous distribution by a process which, on  
the one hand, ensures optimum crease re-  
covery and dimensional stability of the  
treated products, and on the other hand,  
30 reduces to the minimum possible magnitude  
the inevitable reduction in tearing strength  
and abrasion resistance, relative to the start-  
ing material, which accompanies the produc-  
tion of the finish.

- According to the invention there is pro-  
35 vided a process for producing a layered  
finish on the fibres of cellulosic textile fabrics  
wherein the fabrics or fibres from which they  
are to be made are saturated with a water-  
soluble cross-linkable synthetic resin mono-  
40 mer and/or oligomer and a cross-linking  
catalyst so that some of the monomer and/or  
oligomer and catalyst diffuse into the fibres;  
the monomer and/or oligomer and catalyst  
are washed from the surface of the fibres by  
45 means of an aqueous sol of a colloidal sur-  
face-active substance which forms a resilient  
film on the fibres without diffusing into  
them; and the monomer and/or oligomer  
diffused into the fibres and the said sub-  
50 stance are fixed to the fibres by crosslinking  
of the monomer and/or oligomer and dry-  
ing.

- Preferably, a further layer is applied to the  
uppermost layer of the colloidal material by  
55 treating the latter, before fixing, with an  
aqueous solution of compounds suitable for  
making a covalent bond with the colloidal  
material and of the general formula (I)—  
(VI), as shown in the accompanying draw-  
60 ing, wherein R is  $\text{CH}_3$ — $(\text{CH}_2)_n$  and  $n=10$ —  
16.

- As monomer and/or oligomer we prefer  
to employ dimethylol-methylene carbamide,  
dimethylol - dihydroxy - ethylene - car-  
65 bamide, trimethylol - melamine, hydroxy -

ethyl - thiazone, hexamethylol - melamine,  
dimethylol - carbamide or similar monomers  
or oligomers. The cross-linking catalyst may  
be selected from the following group of  
70 compounds:  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  
 $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Zn}(\text{NO}_3)_2$ , ammonium tartrate and  
substances of similar effect.

As surface-active film-forming, colloidal  
materials we prefer to employ protein  
derivatives cross-linked to colloidal form  
75 with aldehydes, carboxymethyl - cellulose,  
cellulose ethers or starch ethers, partially  
acetylated polyvinyl alcohol, methylol  
melamine-based acid colloid, aqueous poly-  
urethane dispersions or other similar  
80 materials. As representative compounds suit-  
able for developing covalent bonds for  
cellulose we mention N - stearyl - acrylamide,  
stearyl - methyl - pyridine - ether, N -  
stearyl - methylamide - methylene - pyridine -  
85 chloride.

The colloidal material may be employed  
in an aqueous preparation which also contains  
the cross-linkable monomer and/or oligomer,  
a cross-linking catalyst, expediently in a con-  
90 centration which amounts to a minimum of  
50% and a maximum of 200% by weight of  
the concentration used in the first saturating  
solution.

We have found it advantageous that the  
95 impregnation with the cross-linkable  
synthetic resin monomer and/or oligomer  
and the catalyst should be performed with a  
padder or with other machine treatment of  
equivalent effect. We proceed similarly for  
100 the treatment with the surface active material,  
and in given cases also with the production  
of the further layer applied to the textile  
product.

A characteristic of the process according  
105 to the invention is that no drying or con-  
densation is required between the individual  
operations performed with different materials,  
in spite of which the desired technical aim  
can be achieved to a greater extent than  
110 hitherto. The material to be treated may be  
e.g. a cotton or bast fibre fabric, hemp, China  
grass or mixtures of these with regenerated  
cellulose, a fabric of cotton mixed with poly-  
ester, regenerated cellulose-based or linen  
115 fabric.

The invention is based on the discovery  
that with the described process discrete  
layers of heterogeneous distribution may be  
120 formed in the cross-section of the filamentary  
material to be treated. To this end the  
simplest solution would appear to be pro-  
vision of directional cross-linking by rinsing  
with an aqueous solution (on the basis of  
125 osmotic pressure) the washing effect of which  
is limited exclusively to the surface of the  
filaments. Since the diffusion of the cross-  
linking monomer during penetration and  
during drying is of opposite effect to the  
rinsing, washing or rinsing, experiments per-  
130

formed with water have not been successful. Attempts have been made, in known manner, to eliminate the difficulties arising from the extremely rapid forward and back diffusion of the monomer, by reducing the swelling of the filament, washing with organic solvents, or using surface catalyst poisons.

We see it as important that we perform the removal of the cross-linking material from the surface layer of the textile product with an aqueous solution with apparatus of limited washing effect. A padder is suitable for this purpose. Performing the removal step of the cross-linking material once or twice, a heterogeneous filament structure may be developed which remains even after the succeeding drying and condensation steps.

Thus, in practising the invention, first the cross-linkable, water-soluble, synthetic resin monomer, and/or the oligomer formed therefrom, and the catalyst are applied by impregnation to the filament or fabric to be treated. Thereafter, suitably without intermediate drying, the cross-linkable, water-soluble component and the catalyst are expelled from the surface of the treated materials by a washing with an aqueous sol of surface-active colloidal material which is water-soluble or dispersible in water, does not diffuse into the material, it is desired to treat, and is resilient and film-forming. The place of the component removed from the filament surface is occupied by the material of colloidal state and size and after the succeeding drying and condensation steps the two components form a heterogeneous, sandwich-type micromolecular system.

With the process according to the invention the abrasion resistance of the surface layer may be improved by applying further resiliency - improving and plasticising materials. One proceeds as follows: after applying the colloidal material to the material to be treated but without interposing a drying step, the uppermost layer of colloidal material applied to the surface is washed off, as by padding with a solution of a surface-active softening substance which is capable of forming a covalent bond with the colloidal material, and thus the colloidal material disposed on the surface is displaced. To apply this further layer compounds specified in the above description are employed.

After application of these various materials the treated product is dried at a temperature of 70—100°C to a moisture content of 5—15%, and condensation is effected in 2—6 minutes at a temperature between 13—160°C. While a following rinsing and drying of the textile material is recommended, this may be deferred until the first aqueous treatment (washing) of the textile material.

The general result of the process according to the invention is that the dry and wet

crease recovery and dimensional stability of cellulose-based filaments or textile products are significantly improved while the abrasion resistance of the filament is good.

The process according to the invention is further described by the following non-limiting Examples.

#### Example 1

Cotton fabric was saturated with a solution of 100—150 g/litre 50% dimethylol - ethylene - carbamide and 10—15 g/litre  $\text{MgCl}_2$  at a temperature between 20—30°C and a pressure efficiency of 85% by a padder at a rate of 30 m/min. Then, without intermediate drying, the treated cotton fabric was padded with a gelatine solution, pretreated with formaldehyde, at 40°C and at the previous rate.

After the padding treatment the treated cotton fabric is dried on a tentering frame at a temperature around 100°C, and condensed for 5 minutes at 140°C.

#### Example 2

Cotton fabric was saturated with a solution of 100—120 g/litre 50% hexamethylol-melamine and 3—5 g/litre  $\text{NH}_4(\text{SO}_4)_2$  at a temperature between 20—30°C using a 85% pressure efficiency on a padder at a rate of 30 m/min. Then, without intermediate drying, the treated cotton fabric was treated in a padder by a 40°C polyvinyl alcohol solution pretreated with 3—5 g/litre formaldehyde.

The treated fabric was subjected to further processing in the manner according to Example 1.

#### Example 3

A mixed fabric of 67% cotton and 33% polyester was padded by a solution of 100—150 g/litre, 50% dimethylol - ethylene - carbamide and 10—15 g/litre magnesium chloride at a temperature between 20—30°C and 85% pressure efficiency. Without intermediate drying a padding treatment was carried out at 40°C with a solution of 1—8 g/litre polyvinyl alcohol pretreated with formaldehyde and 6—24 g/litre magnesium chloride.

The treated fabric was subjected to further processing in the manner according to Example 1.

#### Example 4

A regenerated cellulose-based fabric was treated in a padding apparatus with a solution of 100—150 g/litre, 50% dimethylol - ethylene - carbamide and 10—15 g/litre  $\text{MgCl}_2$  at a temperature between 20—30°C, at a rate of 50 m/min. and 85% pressure efficiency. Then, without intermediate drying, the treated fabric was padded with a solution of 20—100 g/litre acid colloid, pre-

pared as described below, at a temperature between 20—40°C.

- To prepare the acid colloid solution, 300 g 50% trimethylol melamine was mixed with 30 g 85% phosphoric acid, then the mixture was diluted with 600 ml water and heated in a mixer at 50°C for approximately one hour; after adding 50 g trimethylamine the reaction mixture was allowed to cool to room temperature to obtain a colloidal condensate.

- The two layers applied to the regenerated cellulose-based fabric treated as described above were subjected to finishing processes (drying and condensation) according to Example 1.

#### Example 5

A linen fabric was treated according to Example 3, with the difference that after the second padding treatment, without intermediate drying, the treated fabric was further treated with a solution of 50—100 g/litre concentration of N-stearyl acrylamide or a solution of stearyl - methylamido-methylene - pyridine chloride of similar concentration. The final drying and condensing process were carried out according to Example 1.

The improved properties of textile products treated according to the invention are summarised in the following Table:

TABLE

Method of Preparation	Abrasion cycle no. (n)* Stoll	Weight loss % (Accelerator)**	Crease recovery angle in °	
			dry	wet
35 Mercerised and bleached fabric without synthetic resin	3250	6.8	67	73
40 Mercerised and bleached fabric, treated with synthetic resin in the known manner	757	39.5	114	123
40 Mercerised and bleached fabric, treated by process according to the invention	1451	24.1	117	126

\* flexed and abraded in a Stoll QM Abrasion testing machine

\*\* abrasion with Accelerator, three minutes at 3000 r.p.m.; area of abraded surface 136 × 136 mm.

#### WHAT WE CLAIM IS:—

1. A process for producing a layered finish on the fibres of cellulosic textile fabrics wherein the fabrics or fibres from which they are to be made are saturated with a water-soluble cross-linkable synthetic resin monomer and/or oligomer and a cross-linking catalyst so that some of the monomer and/or oligomer and catalyst diffuse into the fibres; the monomer and/or oligomer and catalyst are washed from the surface of the fibres by means of an aqueous sol of a colloidal surface-active substance which forms a resilient film on the fibres without diffusing into them; and the monomer and/or oligomer diffused into the fibres and the said substance are fixed to the fibres by cross-linking of the monomer and/or oligomer and drying.
2. A process as claimed in claim 1 wherein a further layer is applied to the uppermost layer of the colloidal material by treating the latter, before fixing, with an aqueous solution of compounds suitable for making a covalent bond with the colloidal material and of the general formula (I)—(VI), where R is  $\text{CH}_3$ — $(\text{CH}_2)_n$  and  $n=10-16$ .
3. A process as claimed in claim 1 or 2 wherein as monomer dimethylol - ethylene carbamide, dimethylol - dihydroxy - ethylene - carbamide, trimethylol - melamine,

hydroxy - ethyl - thiazone, hexamethylol - melamine, dimethylol - carbamide, or similar monomer, is employed.

4. A process as claimed in any preceding claim wherein as catalyst one or more of the following compounds are employed:  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Zn}(\text{NO}_3)_2$ .

5. A process as claimed in any preceding claim wherein as surface-active, film-forming, colloidal materials protein derivatives cross-linked to colloidal form with aldehydes, carboxyl - methyl - cellulose, cellulose ethers or starch ethers, partially acetylated polyvinyl alcohol, methylol melamine-based acid colloid, or aqueous polyurethane dispersions, are used.

6. A process as claimed in claim 2 or any claim appendant thereto, wherein the material suitable for forming covalent bonds with the filamentary material is chosen from N - stearyl - acrylamide, stearyl - methyl - pyridine - ether or N - stearyl - methylamide - methylene - pyridine - chloride.

7. A process as claimed in any preceding claim wherein a colloidal aqueous preparation of the surface active substance is employed which, in addition to the cross-linkable synthetic resin monomer and/or oligomer, also contains a cross-linking catalyst, in a concentration which amounts to a minimum of 50% and a maximum of 200% by weight

of the concentration used in the first saturating solution.

- 5 8. A process as claimed in any preceding claim wherein the treatment (impregnation) with the cross-linkable synthetic resin monomer and/or oligomer and catalyst is carried out by padding.

- 10 9. A process as claimed in any preceding claim wherein the treatment with the surface-active material is carried out by padding.

- 10 10. A process according to claim 2 or any claim appendant thereto, wherein the further layer is applied to the material to be treated by padding.

- 15 11. A process as claimed in any preceding claim wherein consecutive layer-applying steps are carried out without intermediate drying and condensation.

- 20 12. A process as claimed in any preceding claim wherein the material to be treated is any one of cotton fabric, a mixed fabric of

cotton and polyester, regenerated cellulose-based fabric or linen fabric.

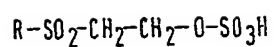
13. A process as claimed in any of claims 8 to 12 wherein the padding is carried out at a rate of 30—150 m/min. 25

14. A process as claimed in claim 1 substantially as herein described with reference to the Example.

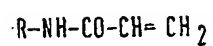
15. A textile product having a finish produced by a process as claimed in any preceding claim. 30

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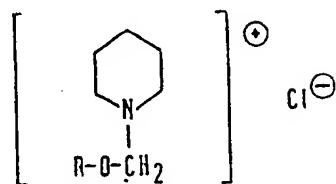
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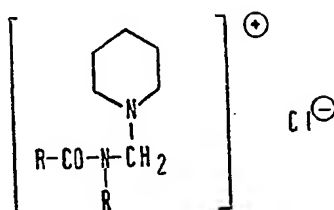
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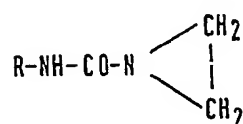
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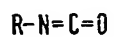
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